Dendrite-Growth Morphology Modeling in Liquid and Solid Electrolytes

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General Motors R&D Center

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Project ID: bat328

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Overview

Timeline

- Project start date: 01/01/2017
- Project end date: 12/31/2019
- Percent completed: 35%

Barriers

Li metal film electrodes with

- Dendrite growth
- Low coulombic efficiency
- Short calendar and cycle life

Budget

- Total project funding: $1,135,125
  - DOE share: $999,943
  - Contractor share: $135,182

Partners

- Interactions/collaborations
  - Gary Rubloff (UMD) :
    Coating development
  - Katherine Jungjohann : SNL-ALBQ
    In situ TEM, liquid cell
- Project lead, Yue Qi (MSU)

Relevance / Objectives

Overall Objective

- Develop a validated multi-scale model to predict Li dendrite morphology evolution in both liquid and solid electrolytes LIBs during electrodeposition and stripping, in order to ***accelerate the adoption of Li metal electrodes in current and emerging battery technologies.***

Technical Target

- An atomically-informed, fully-coupled electrochemical-mechanical dendrite morphology evolution model that allows us to design the desired properties of artificial SEI coatings, the microstructure of solid electrolyte materials, and the corresponding battery operating conditions, so as to avoid dendrite growth during cycling.

Impacts

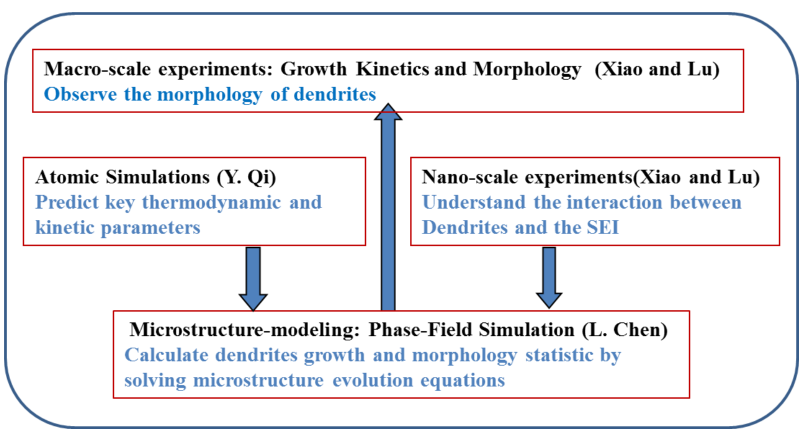
- Enable the design of durable and safe Li-anodes for high energy density lithium rechargeable batteries that can meet DOE's target for EV applications >350 Wh/kg & <$100/kWh$_{use}$.

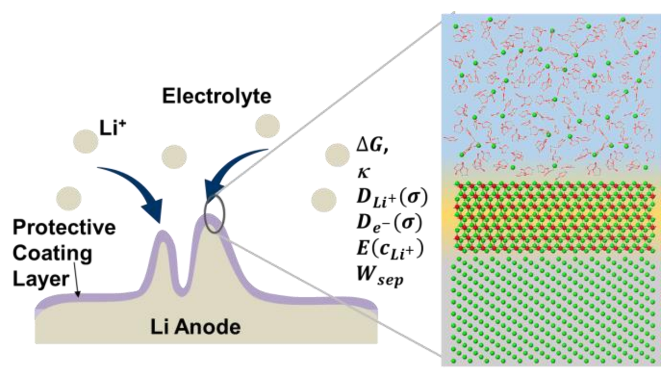
2018 Milestones

Month /Year	Milestone of Go/No-Go Decision	Status
Dec. 2017	Determine if the effect of SEI on dendrite growth should be modeled implicitly or explicitly (GO/NO-GO)	Go
Mar. 2018	Identity the electronic pathway of Li dendrite growth inside LLZO.	80% completed
Jun. 2018	Identify the Li ion pathway of Li dendrite growth inside LLZO	In progress
Sep. 2018	Develop a multiphase multigrain phase-field model, that incorporates the mechanical and electrochemical driving forces for Li dendrite growth in polycrystalline solid electrolyte	In progress

Multiscale Modeling and Experimental Approach

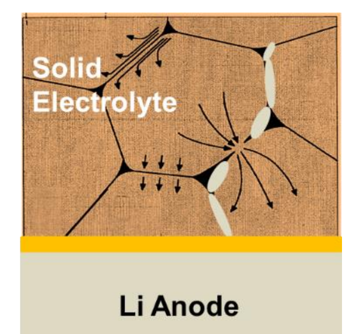
- **Formulate** a general framework that captures the electrochemical-mechanical driving forces for Li morphology evolution.
- **Consider** the role of the *nm-thin SEI* in liquid-electrolytes as well as the microstructures of *μm-thick* solid-electrolytes for Li morphology evolution.
- **Connect** micron-scale phase-field models and atomic-scale DFT-based simulations via parameter- and relationship-passing in order to predict *Li dendrite nucleation and growth kinetics and morphology*.
- **Validate** the key input parameters and main conclusions of the multi-scale model as new capabilities being developed step-by-step.





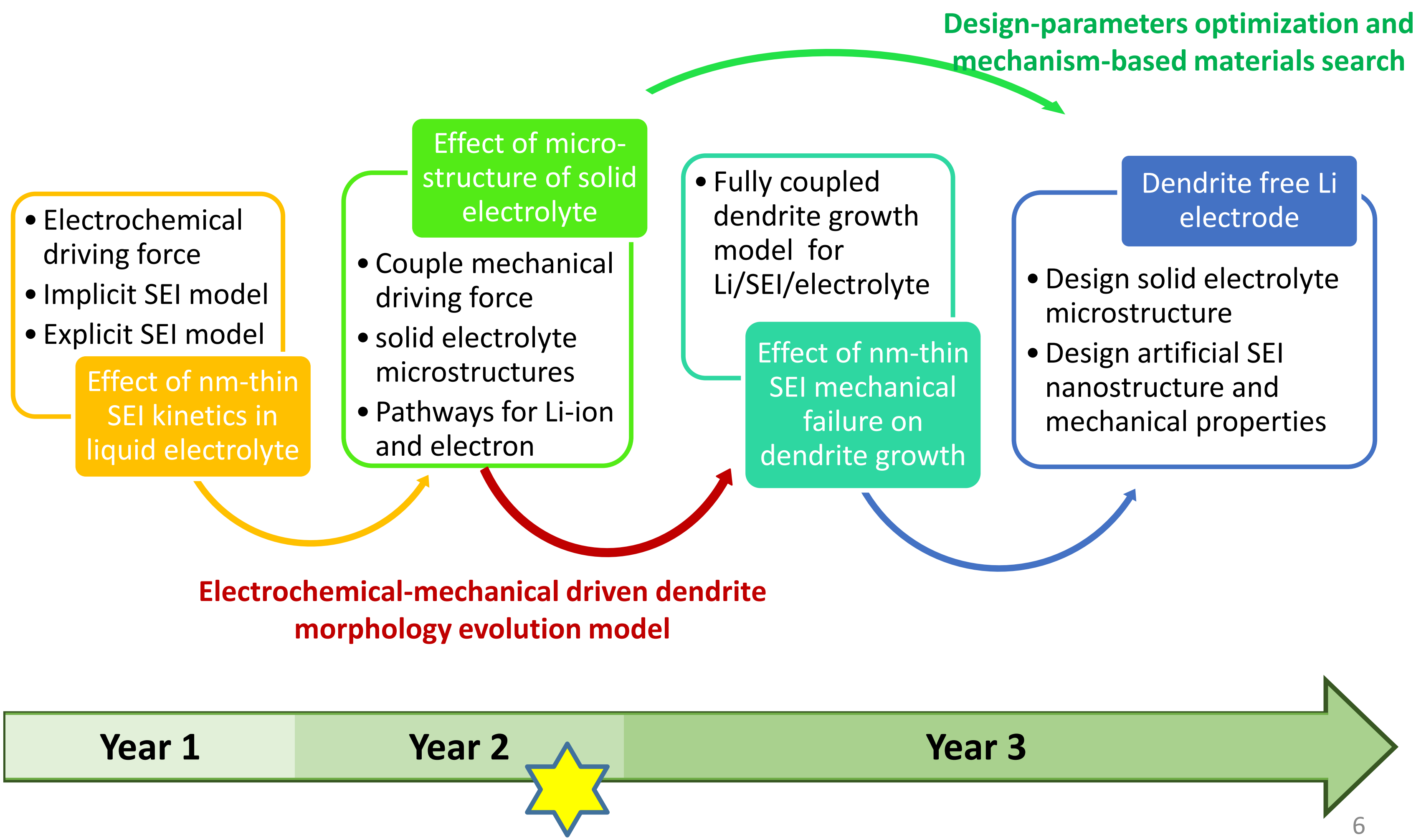
Phase field modeling

DFT & DFTB modeling



Model Development Strategy and Timeline

Model liquid and solid electrolytes in order to couple electrochemical-mechanical driven dendrite growth step-by-step



Outline and the Accomplishments

- An implicit multiscale dendrite growth model is developed
  - Developed a half-cell model to compute the charge transfer reaction energy landscape and kinetics at a Li/SEI/electrolyte interface from DFT-DFTB simulations
  - Reformulated the phase field model to directly couple Butler-Volmer equation with atomistic predictions and the effect of SEI layer on charge transfer reaction.
  - Compared the morphological difference of Li-plating vs Mg-plating
  - Performed parametric study to achieve flat surfaces during Li plating
  - Experimentally vary the interface kinetics through surface engineering

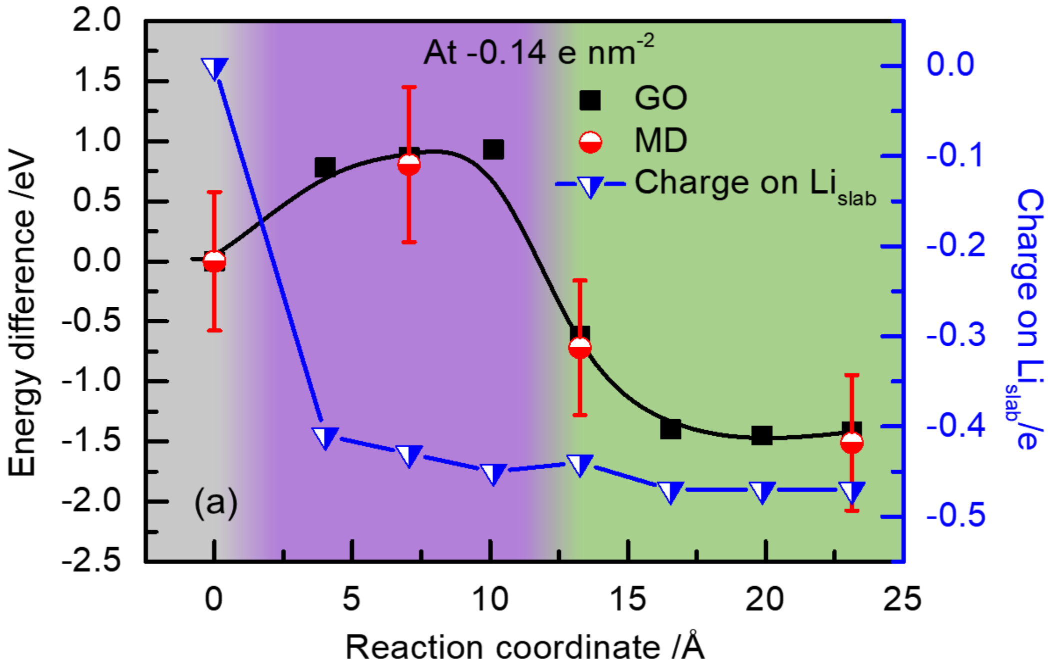
- Constructed a new explicit model to simulate Li dendrite formation and growth in a solid electrolytes with microstructure and internal defects (pores)
  - Evaluated the metallic Li nucleation tendency on pore surfaces in solid electrolyte (LLZO) with DFT calculations.
  - Proposed an interlayer material (ALD-Li_2PO_2N coating) to suppress Li-dendrite
  - The Phase field model is developed to incorporate the microstructure of solid electrolytes with coupled electrochemical-mechanical driving forces

Accomplishment 1.1: Developed a half-cell model & Demonstrated that the charge transfer reaction occurs under the perfect SEI

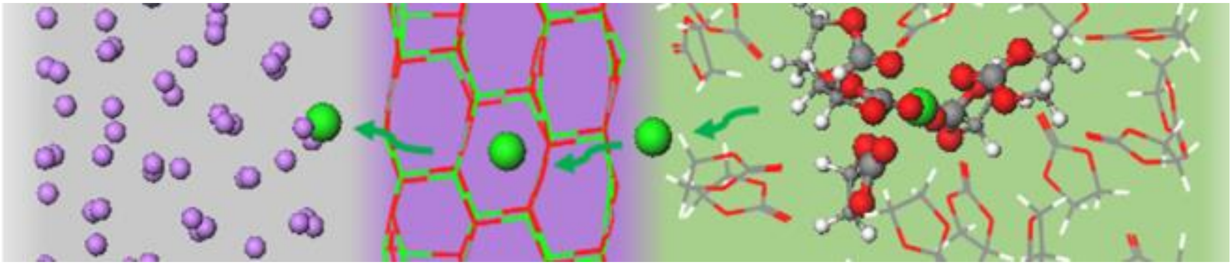
Electrochemical reaction $Li^{+}(sol) + e^{-} \rightarrow Li^{0}$ $\Delta G(\sigma_1) = 1.4eV$

Close to thermodynamics cycle prediction 1.2eV

DFTB/DFT calculations



Half Cell model

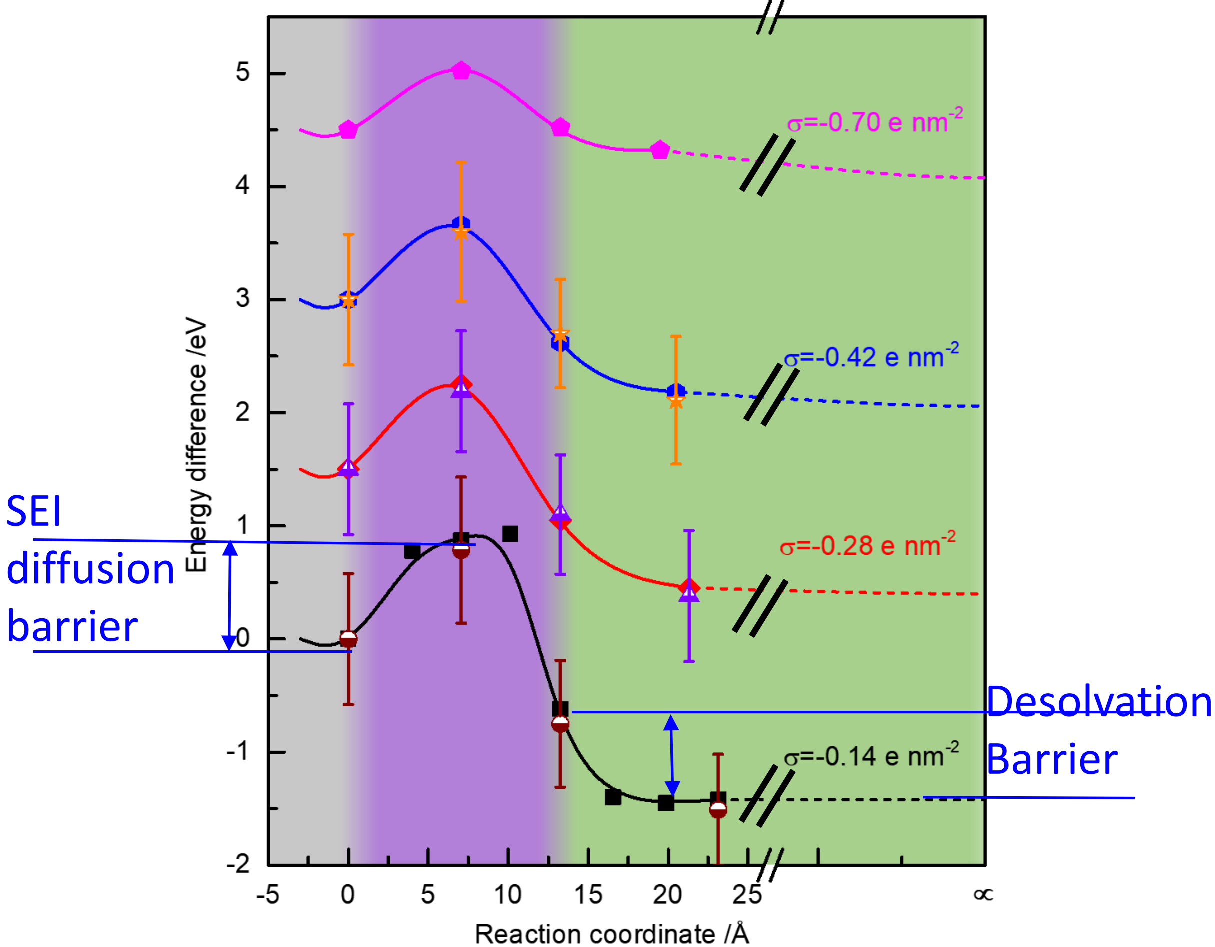


Accomplishment 1.2: Predict the reaction energy and kinetics of Li ion transporting through the SEI layer.

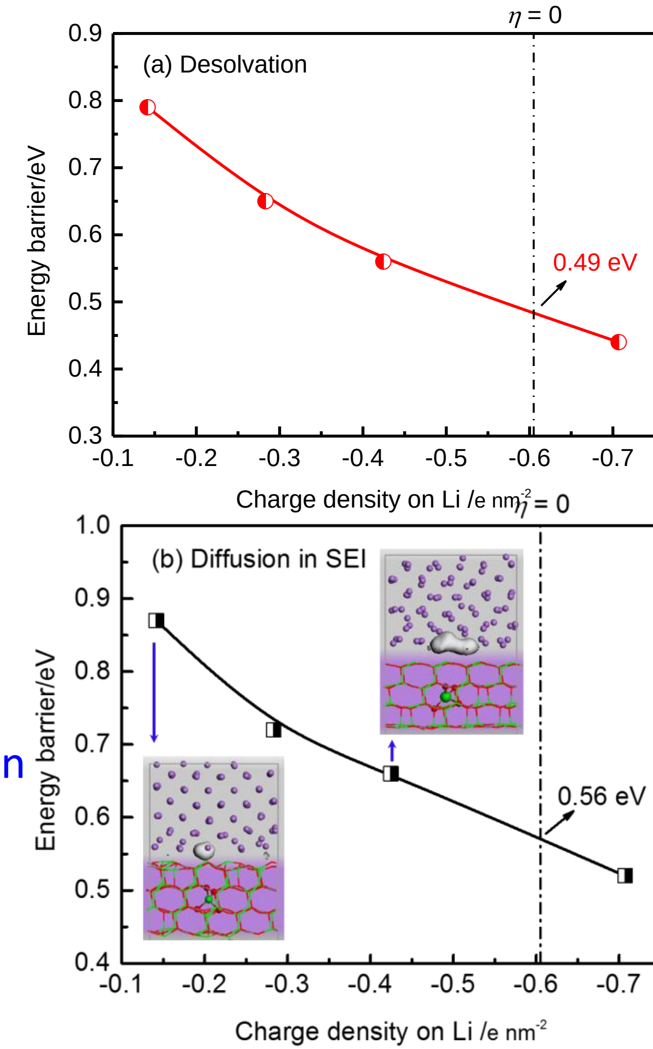
Equilibrium condition

φ^{o} = -1.1V, η=0, σ~ 0.6 e/nm^2

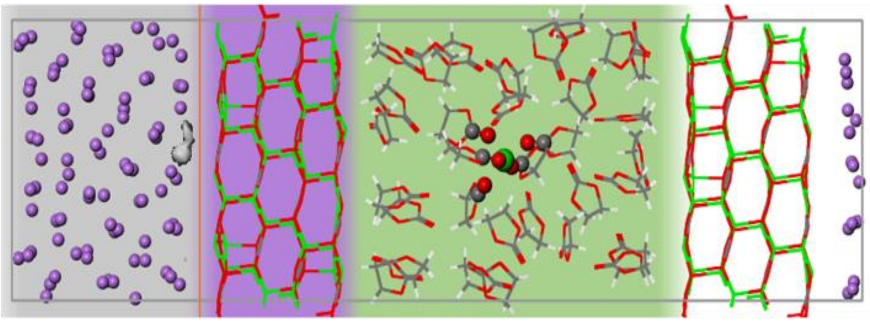
(depending on DFT or DFTB)



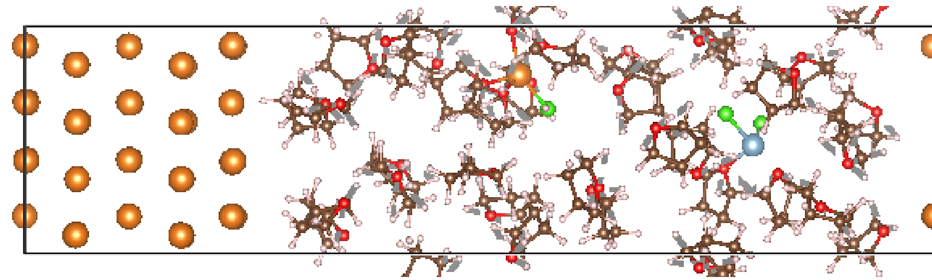
Two Barriers: (Desolvation and SEI diffusion barriers) vary with potential



Accomplishment 1.3: Reformulated the phase field model to directly couple Butler-Volmer equation with atomistic predictions and the effect of SEI layer on charge transfer reactions.



Li $\qquad$ Li^{+}+32EC



Mg $\qquad$ $MgCl^{+}$+$AlCl_2$+32THF

DFTB/DFT calculations of Mg are in progress

Rewrite exchange current

$$I_0^{Li} = \left[\theta_v{}^{N_{Li}} \exp\left(-\frac{\Delta E_{ads}^{Li} + \Delta E_{sol}^{Li}}{RT}\right)\right] eAR_0^{Li} c_{Li^+} \propto A_0^{Li} \theta_v{}^{N_{Li}} \exp\left(-\frac{\Delta E_{sol}^{Li}}{RT}\right)$$

$$I_0^{Mg} = \left[\theta_v{}^{N_{Mg}} \exp\left(-\frac{\Delta E_{ads}^{Mg} + \Delta E_{sol}^{Mg}}{RT}\right)\right] 2eAR_0^{Mg} c_{Mg^{2+}} \propto 2A_0^{Li} \theta_v{}^{N_{Mg}} \exp\left(-\frac{\Delta E_{sol}^{Mg}}{RT}\right)$$

Given $\Delta E_{sol}^{Li} \cong \frac{1}{4} \Delta E_{sol}^{Mg}$ $\qquad$ Therefore, $I_0^{Li} > I_0^{Mg}$

1) Dilute electrolyte solution, $a_{M^{n+}} \cong c_{M^{n+}}$.
2) Electrodeposition is diffusion-limited process, thus electron always supplied at electrode/electrolyte interface, $a_e = 1$.
3) The activity of M atom is constant and can be factored out into R_0.

Accomplishment 1.3: Reformulated the phase field model to directly couple Butler-Volmer equation with atomistic predictions and the effect of SEI layer on charge transfer reactions.

Morphology difference of Li vs Mg (constant Voltage model)

Evolution equation:

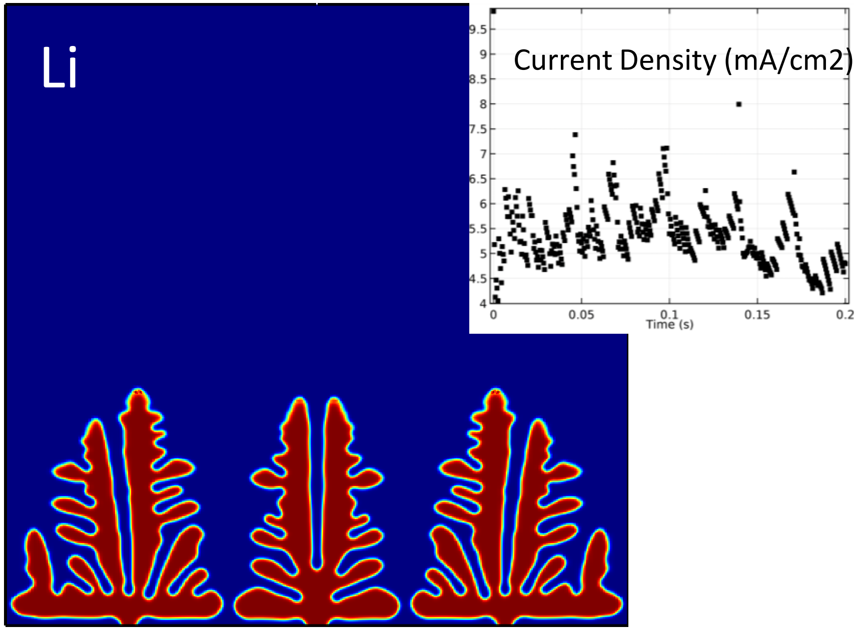
$$\frac{\partial \xi}{\partial t} = -L_\sigma\left(g'(\xi) - \boxed{\kappa}\nabla^2\xi\right) - \boxed{L_\eta} h'(\xi)\left\{\exp\left[\frac{(1-\alpha)\boxed{n}F\eta}{RT}\right] - c_+ \exp\left[\frac{-\alpha \boxed{n}F\eta}{RT}\right]\right\}$$

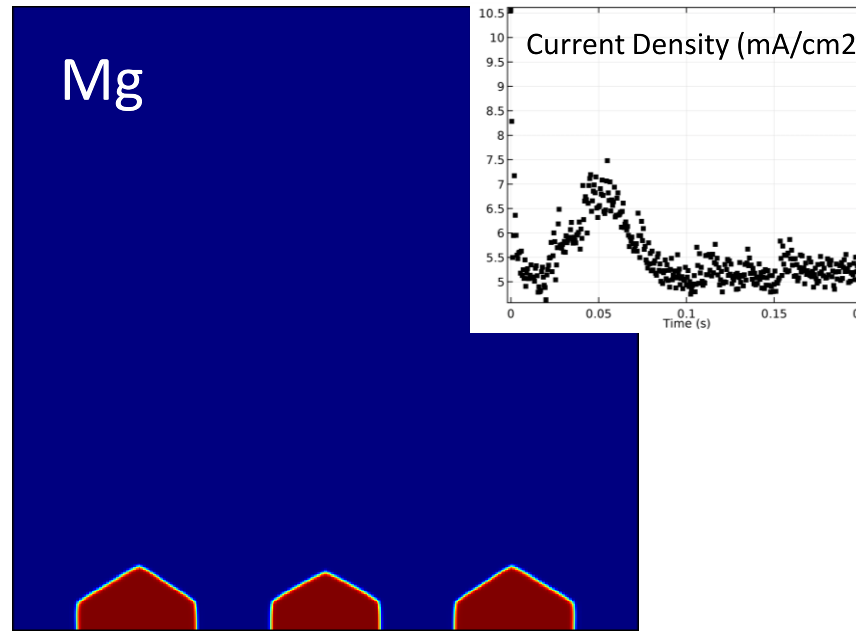
1) Energy gradient coefficient $\kappa(\theta) = \kappa_0[1 + \delta cos(\omega\theta)]$: κ_0-averaged surface/interfacial energy; δ-surface/interfacial energy anisotropy; ω-growth crystallographic symmetry.
2) Electrochemical coefficient $L_\eta = \frac{I_0}{neA}$: I_0-exchange current.
3) Charge transfer electron # n.

Huang *et. al.*, *Advanced Materials Research*, 2012. Liu *et. al.*, *J. Electrochem. Soc.*, 2016.

Physics	Surface energy (J/m2)	Anisotropy	Symmetry	Exchange current	Charge-transfer #
Related parameters	κ_0	δ	ω	I_0	n
Mg	0.73	0.01	6 (hcp)	low	2
Li	0.49	0.03	4 (bcc)	high	1

Accomplishment 1.4: The Implicit dendrite growht model captured the difference between Li and Mg plating





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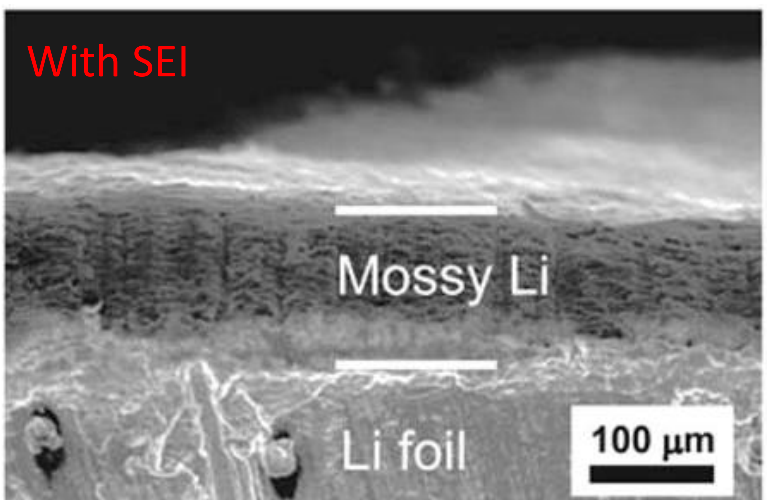

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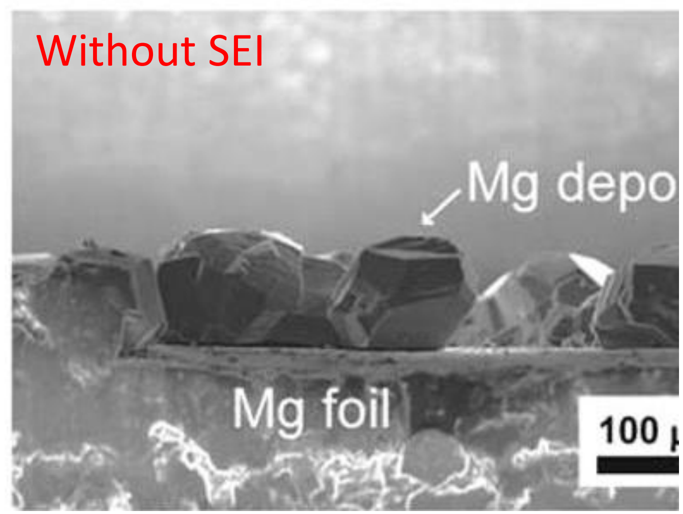
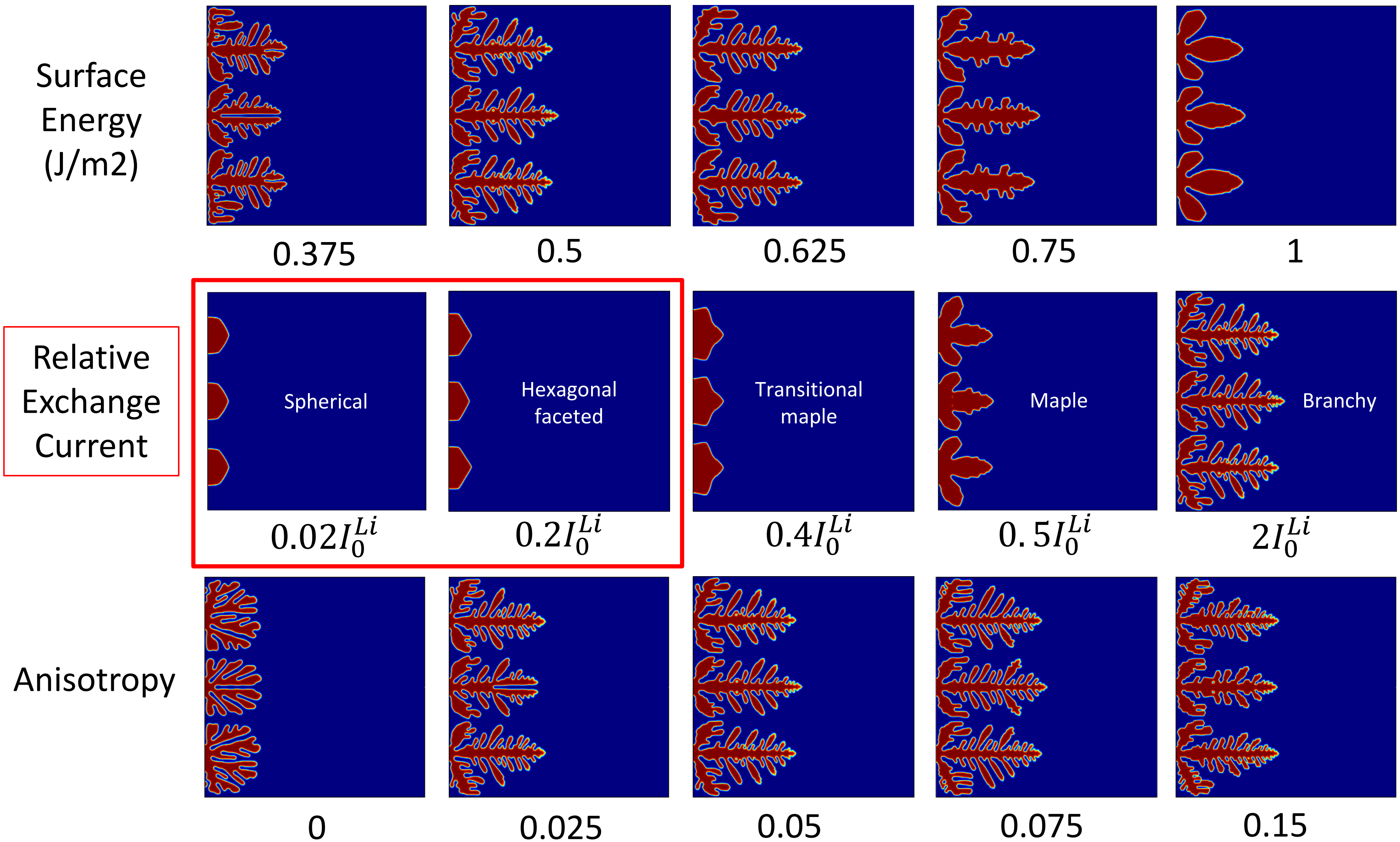


Image: HD Yoo, Y. Liang, Y. Li, and Y. Yao, ACS Applied Materials & Interface, 7 (2015) 7001

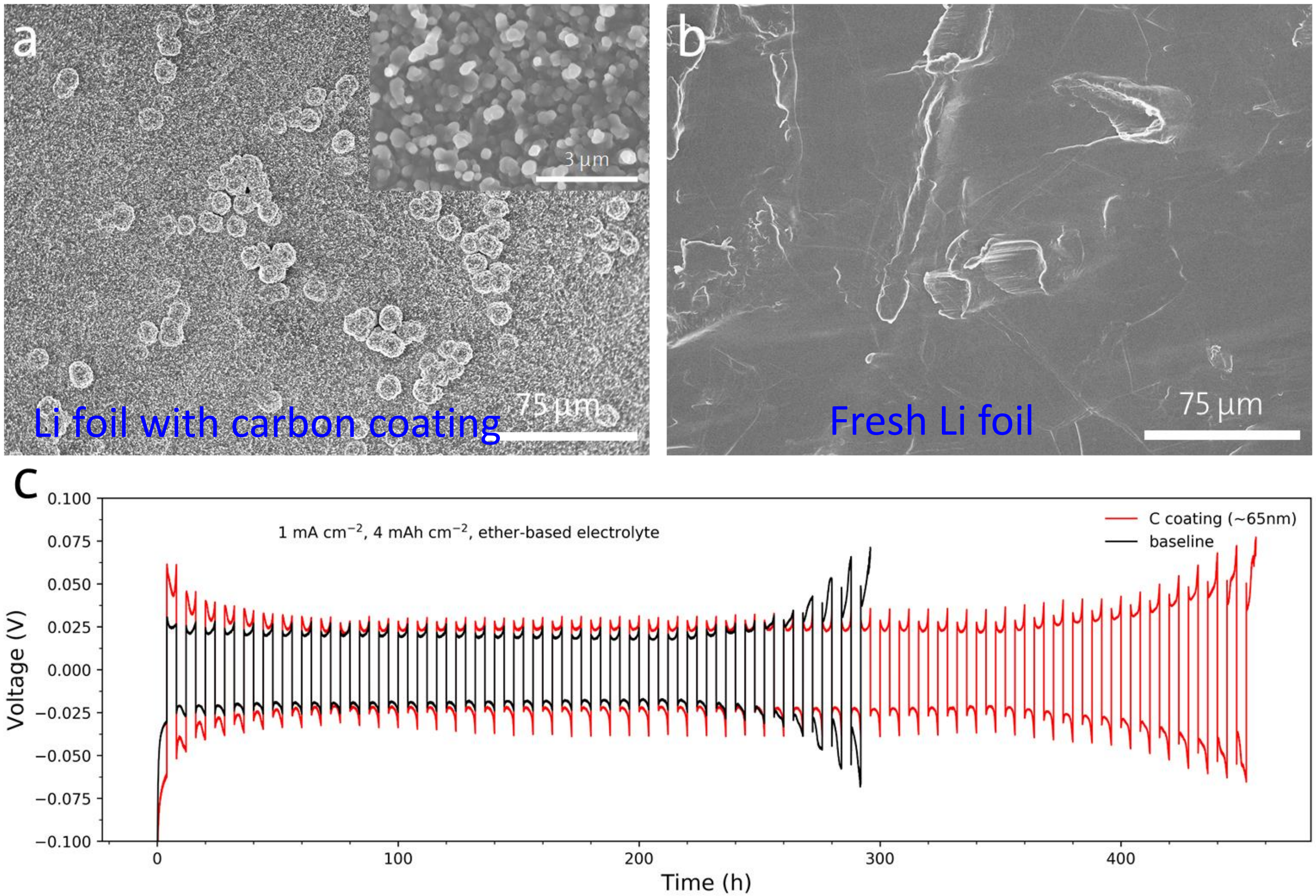
Accomplishment 1.5, Parametric analysis revealed reducing I_0 can achieve Li dendrite-free electrodeposition



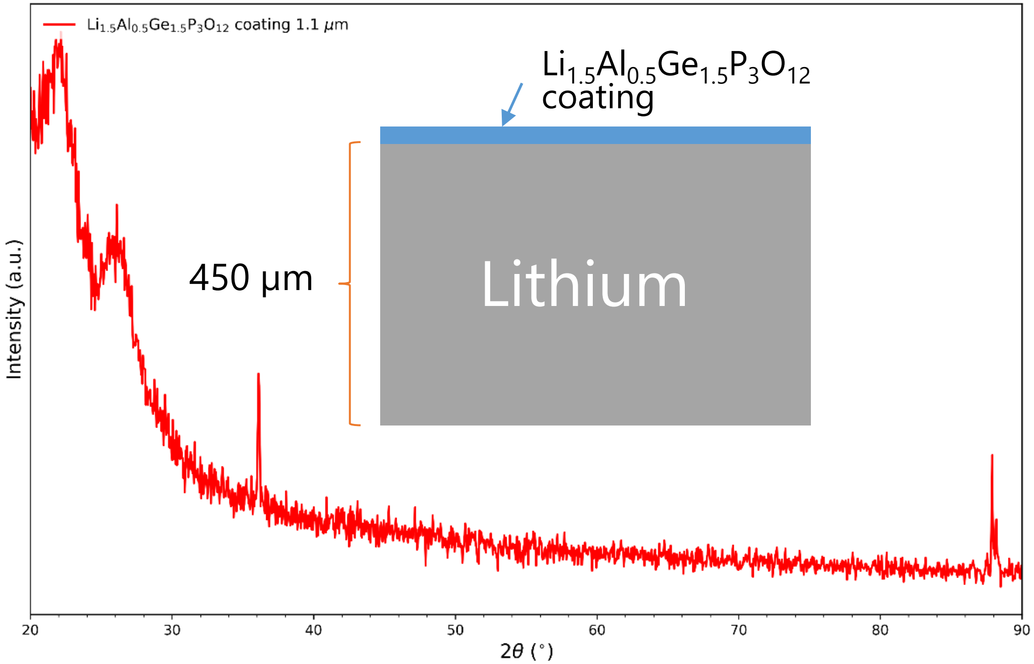
Final morphologies with controlled voltage applied at boundary

Accomplishment 2.1: Experimentally Tune the I_0 via Surface Engineering (electron conductivity)

- The positive effect of ~65 nm carbon coating (DC magnetron sputtered) on improving the cycling stability of lithium metal electrodes was observed recently.
- Uniform carbon coating without cracks was obtained, even though there are some large spherical carbon agglomerates spreading on the surface.



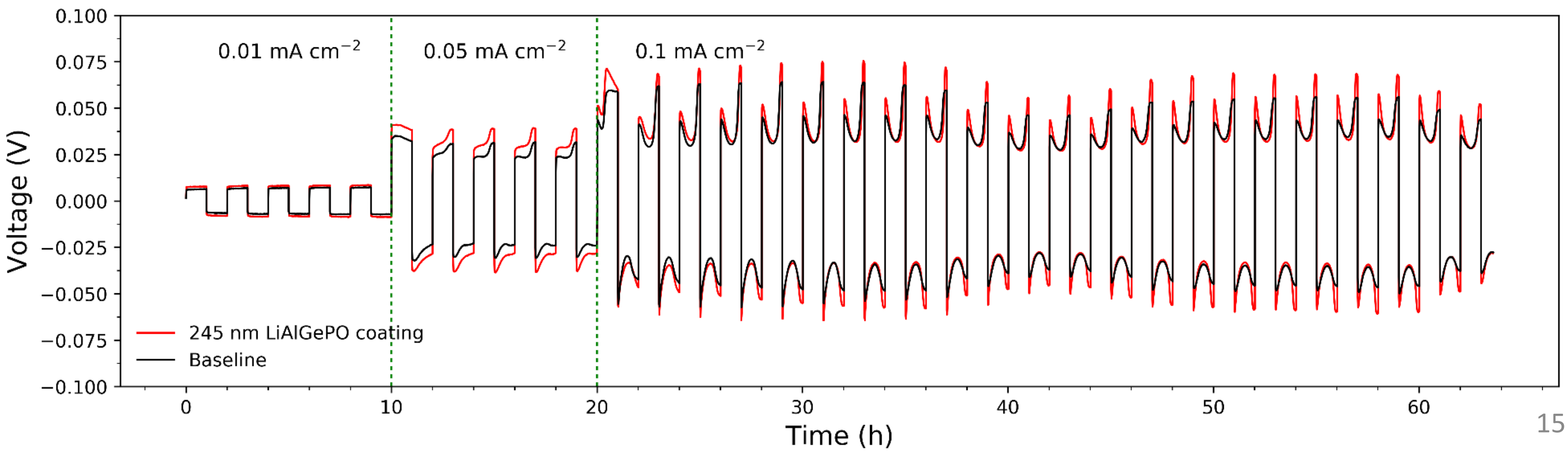
Accomplishment 2.2: Experimentally Tune the I_0 via Surface Engineering (ionic conductivity)



Amorphous $Li_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$ RF coating (thickness: 1.1 μm) is applied via RF magnetron sputtering.

It's expected to promote Li-ion diffusion and isolate the Li-metal from the EC-based electrolyte

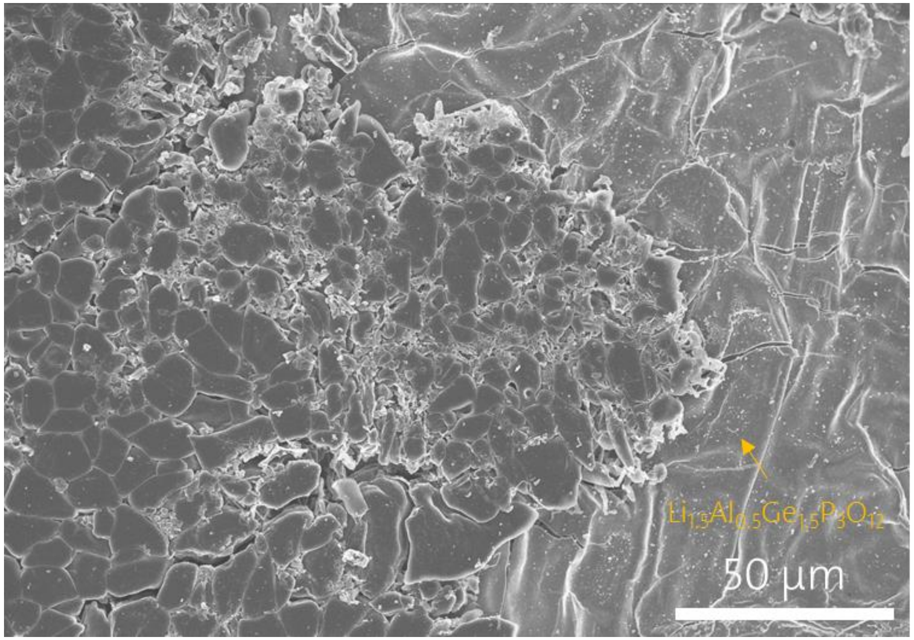
Li-Li symmetric cells test

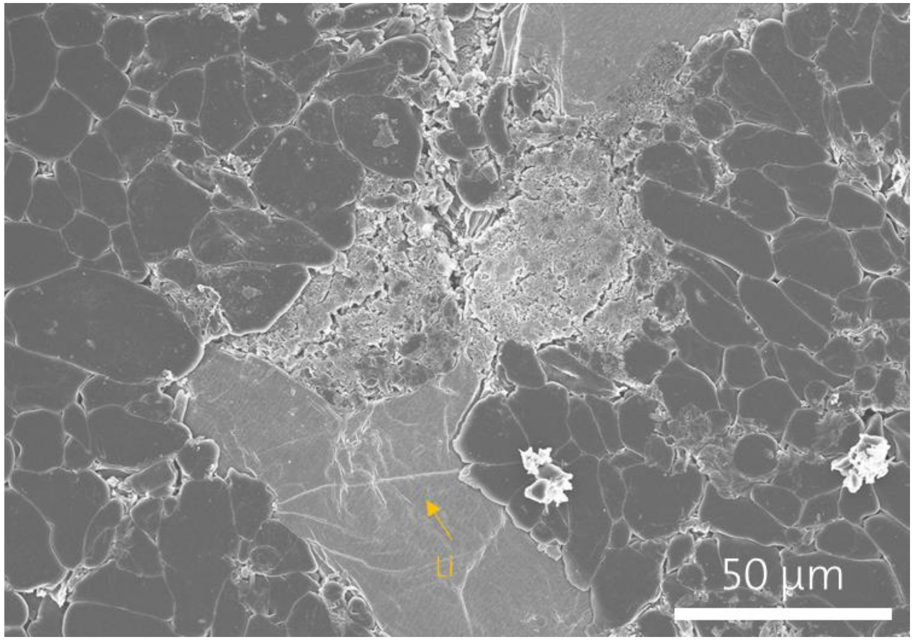


$Li_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$ *coating (245 nm) after cycling*

- Did not show much improvement
- Lithium mossy structures grew outside of the LiAlGePO coating.
- Cracks of coating were observed.

After cycling at 0.1 mA cm^{-2}, 0.1 mAh cm^{-2} in 1 M $LiPF_6$ EC-DEC-FEC





Accomplishment 3.1: Address the driving force for Li plating in Solid Electrolyte

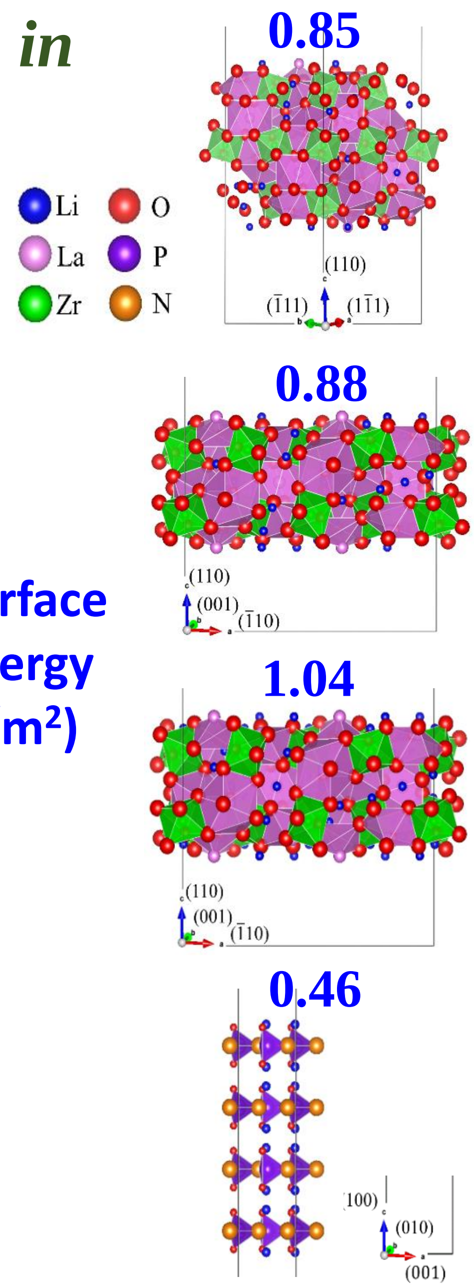
- Assumes there are (pore and crack) surfaces inside solid electrolyte LLZO, or interlayers (ex: t-LLZO and ALD-LiPON)
- Determine the surface structure via DFT calculations
- Analyze the density of states (DOS)

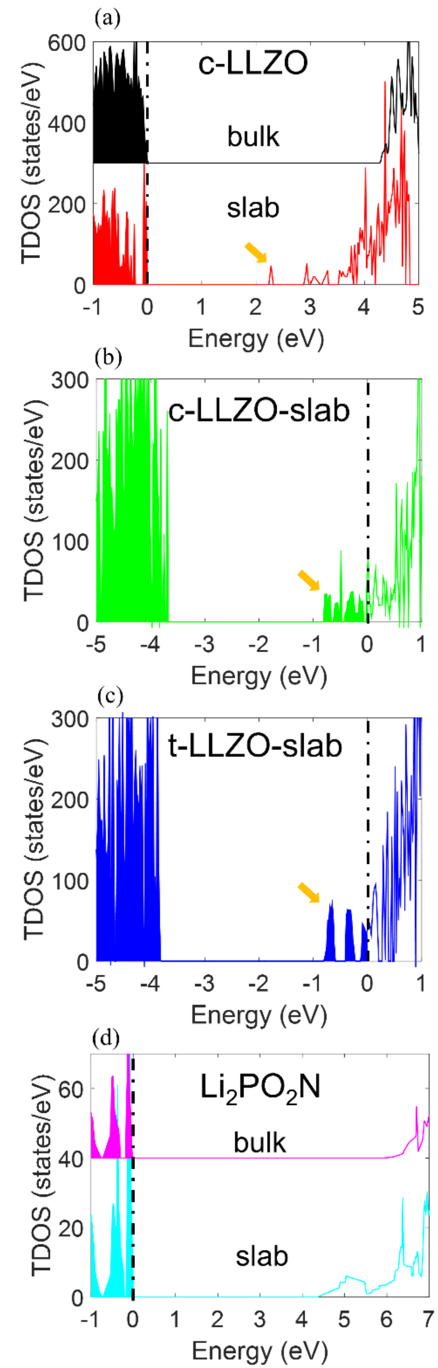
→ Additional surface electronic states appeared the bandgap for all three LLZO structures, but not in Li_2PO_2N.

→ Excess electrons can localize on the La on the surface

→ Compare the formation energy, La_2O_3 is more stable than Li_2O, so Li^+ is likely to be reduced rather than La^{3+} ions by the excess electrons.

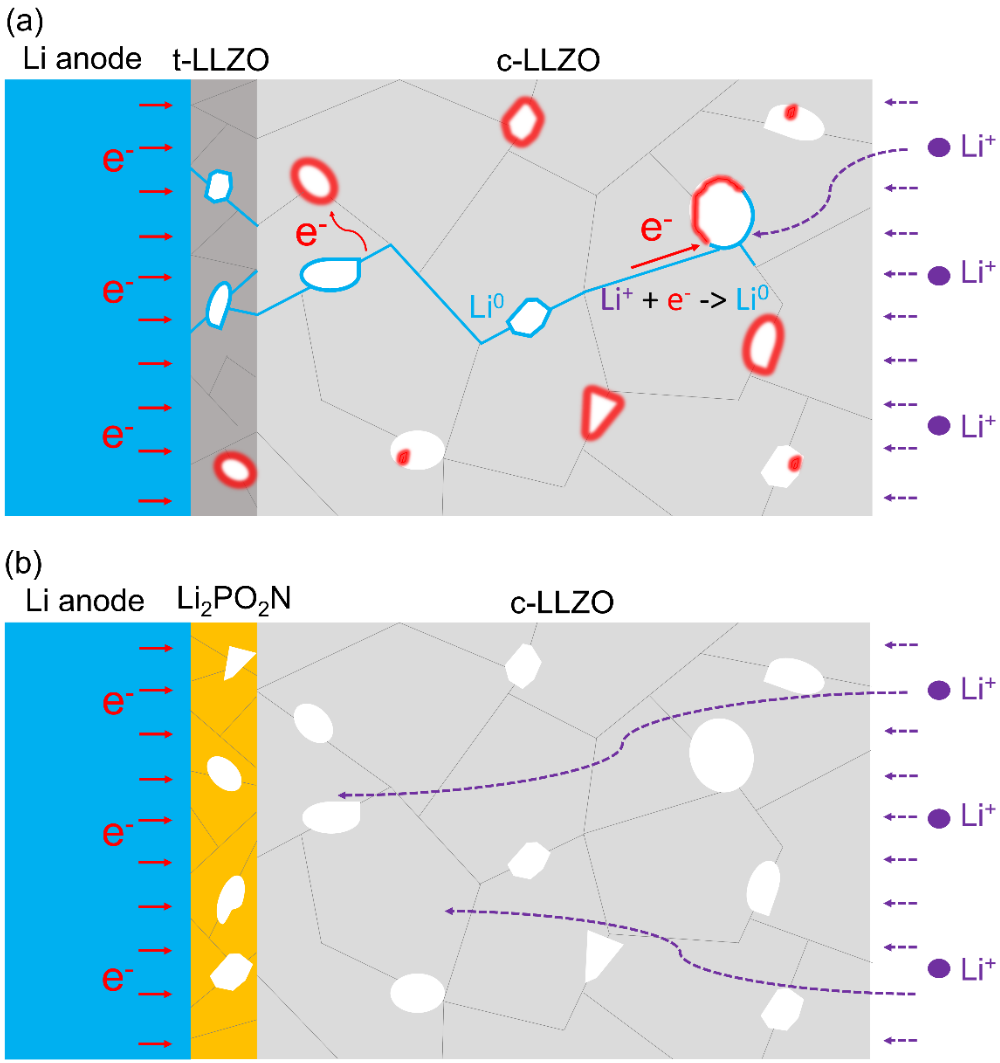
Surface Energy (J/m^2)

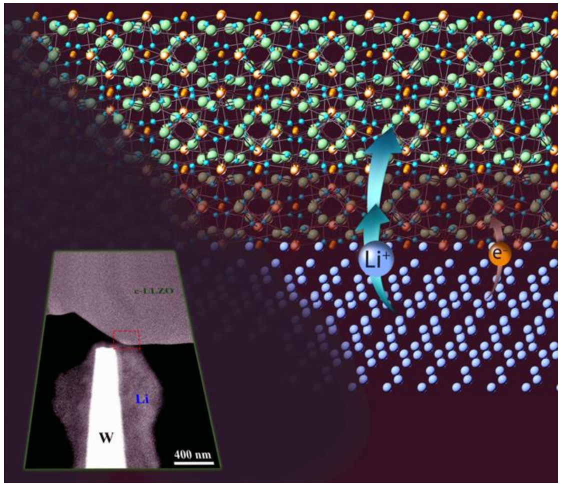




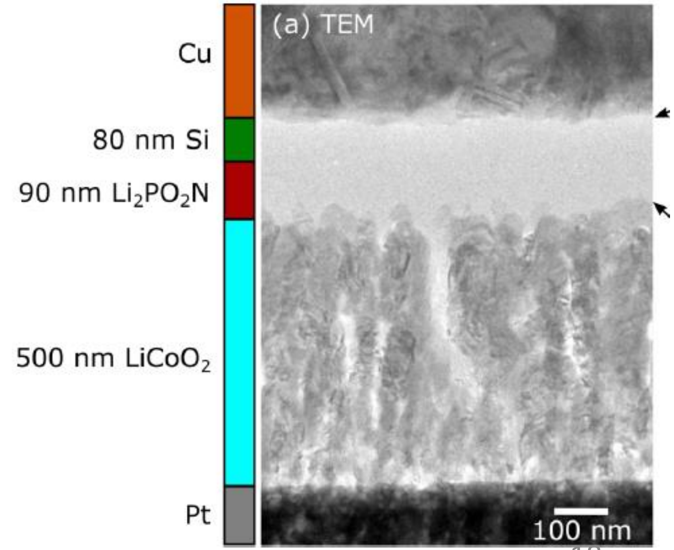
Accomplishment 3.2: Suggest that ALD-Li_2PO_2N may be more efficient to prevent metallic Li nucleation

Nano Lett., **16** (11), 7030-7036 (2016)





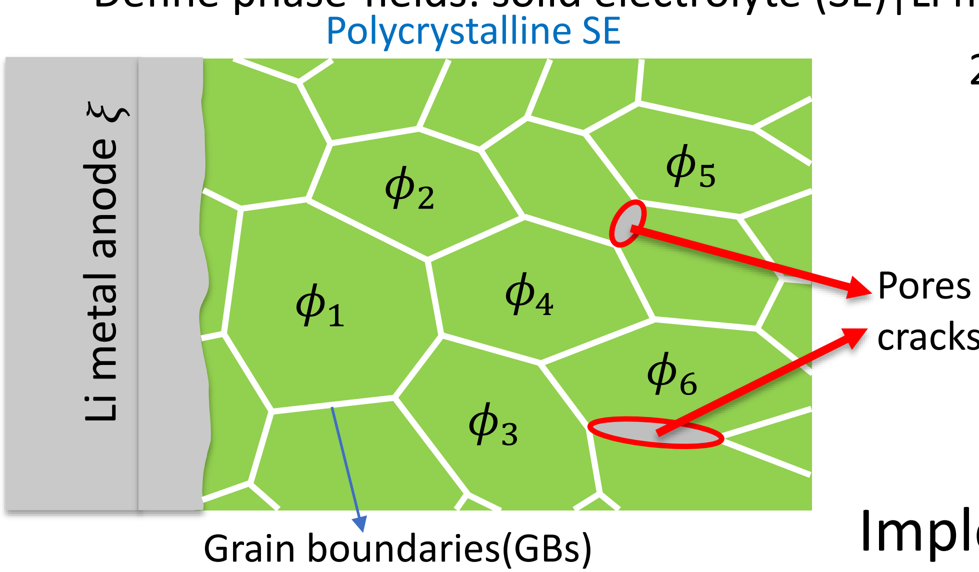
Chem. Mat., **27** (15), 5324-5331 (2015).



Rubloff, UMD, NEES EFRC collaboration

Achievement 3.3 Developed the Phase field model to incorporate the microstructure of solid electrolytes with coupled electrochemical-mechanical driving forces

Define phase-fields: solid electrolyte (SE)|Li metal anode $Li^{+} + e^{-} \rightarrow Li(s)$



2 non-conserved order parameters

Li metal	Pores and cracks
$\xi = 1$	$\xi = 0$
$\phi_i = 0$	$\phi_i = 0$

Solid Electrolyte (multi-grain)

$\xi = 0$

$\phi_1, \phi_2, \phi_3, \ldots \phi_i = (0,0,\ldots,1)$

Implemented elasticity coupling

Tests of elasticity impacts on morphology evolution during Li plating


Mono-grain SE


Straight GB

Phase evolution equation

$$\frac{\partial \xi}{\partial t} = -L_{\sigma}^{\xi}\left[\frac{\partial f_{ch}}{\partial \xi} - \kappa_{\xi}\nabla^{2}\xi + \frac{\partial f_{mech}}{\partial \xi}\right] + \boxed{R_{electrochem}}$$

Achievement 3.4 Revealed that increasing modulus along cannot fully stop Li dendrite growth

Young's Modulus	$E_{Li} = 4.9GPa$	$E_{LLZO} = 150GPa = 30E_{Li}$
Poisson ratio	$\nu_{Li} = 0.362$	$\nu_{LLZO} = 0.257$
Mass density	$\rho_{Li} = 0.534g/cm^3$	$\rho_{LLZO} = 5.34g/cm^3$

Consider constant electrochemical driving force $R_{electrochem}$ for tests

Mono-grain

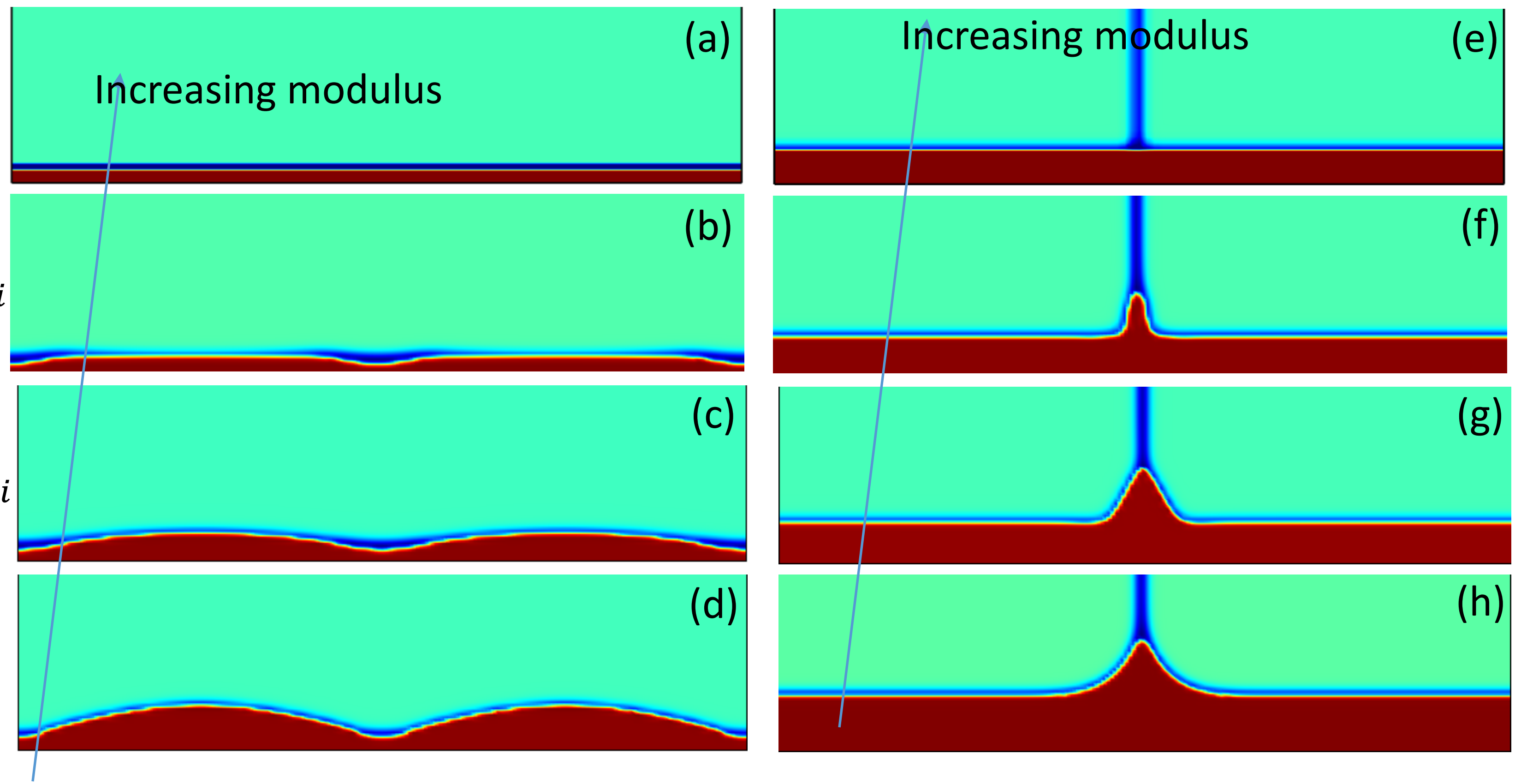
Bi-grain (GB) / similar to crack

Initial

$E_{SE} = 30E_{Li}$

$E_{SE} = 15E_{Li}$

$E_{SE} = E_{Li}$



Increasing elastic modulus resists Li metal mechanical instability (agree with Newman's model)

Increasing elastic modulus leads to less GB splitting angle

Responses to Previous Year Reviewers' Comments

New project started on 1/1/2017.

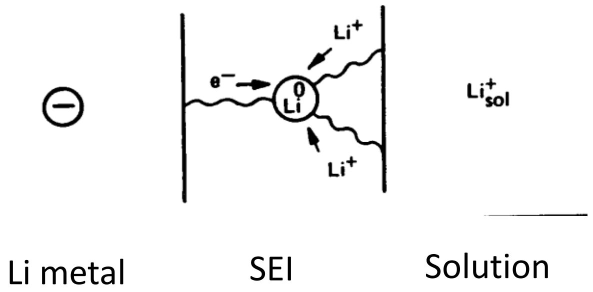
Not reviewed last year.

Collaboration and Coordination with Other Institutions

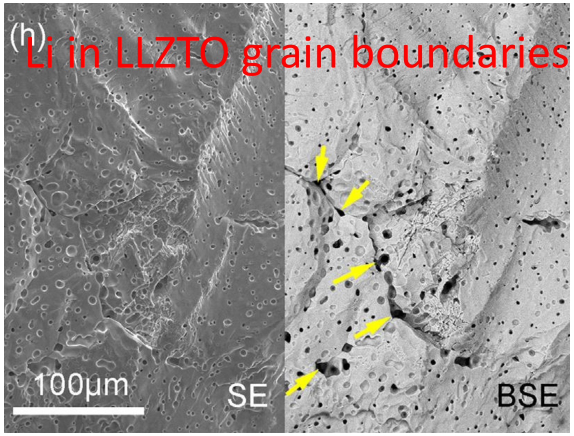
Gary Rublof University of Maryland (DOE NEES EFRC)	Apply ALD LIPON coating, which has higher Li conductivity compared to typical SEI components, such as (LiF, Li_2O, Li_2CO_3), so the thickness and mechanical compliance of the artificial SEI can be investigated.
Katherine Jungjohann SNL-ALBQ (DOE NEES EFRC & CINT)	Investigate the Li morphology using sealed liquid cell for in situ scanning transmission electron microscopy (STEM), and investigate the effect of artificial SEI coating on morphology at nano-meter scale .
Yan Yao University of Houston	Compare Li and Mg plating morphology
Jie Xiao PNNL and U. Arkansas	Investigate the effect electrolyte additives and their role on SEI.

Remaining Challenges and Barriers

- What is the correlation of SEI transport and mechanical property with Li dendrite morphology?
- How to obtain accurate properties of SEI?
- Why and how does Li grow through the mm thick solid electrolyte?
- Can we avoid Li dendrite growth in solid electrolyte by microstructure design?
- Can we take the solid electrolyte microstructure design idea into nm-thick artificial SEI design?



E. Peled, *Lithium batteries, edited by Jean-Paul Gabano.* ***198****3, Publisher: London, Academic Press,*



Y. Ren et. al, Electrochemistry Communications 2015, 57, 27

Proposed Future Research

- Correlate SEI properties with Li dendrite morphology in a liquid electrolyte
- Develop an explicit SEI dendrite growth model to capture the internal structures of SEI.
- Investigate the electrochemical-mechanical-structural coupling effects and explore the mechanism of Li dendrite formation in solid electrolytes from phase field model
  - Explore other solid electrolytes with low Li-metal nucleation tendency
  - Incorporate the mechanical and electrochemical driving forces for Li dendrite growth in solid electrolytes.
  - Experimentally vary the microstructure and porosity of solid electrolytes and observe the corresponding dendrite morphology.
- Modeling and Experiments jointly design effective combinations (bulk solid electrolyte and surface coating) to improve the cycling efficiency and life of lithium rechargeable batteries.

Conclusions

- An implicit multiscale dendrite growth model is developed
  - At the experimentally defined zero volt for Li plating, the Li is already negatively charged at an electric potential about -1V.
  - The desolvation barrier decreases and the Li ion interstitial formation energy (main barrier for Li+ through SEI) decreases with the applied potential.
  - For Li plating to achieve a smooth surface, lowering the exchange current I_0 is the most efficient method.
  - Depositing electronically conductive carbon coating seems to be beneficial.
  - Depositing ionically conductivity solid electrolyte coating layer has no effect, probably due to cracking.

- Constructed a new explicit model to simulate Li dendrite formation and growth in solid electrolytes with microstructure and internal defects (pores)
  - The pore surface in LLZO solid electrolyte can trap excess electron, which is initially located on La^{3+}, however, La^{3+} is thermodynamically more stable than Li^+ based on formation energy calculations, so Li^+ will be reduced.
  - ALD-Li_2PO_2N coating doesn't have surface states to trap excess electrons, thus can be an interlayer at the Li/c-LLZO interface to suppress Li-dendrite
  - Increasing modulus alone cannot stop Li dendrite growth.

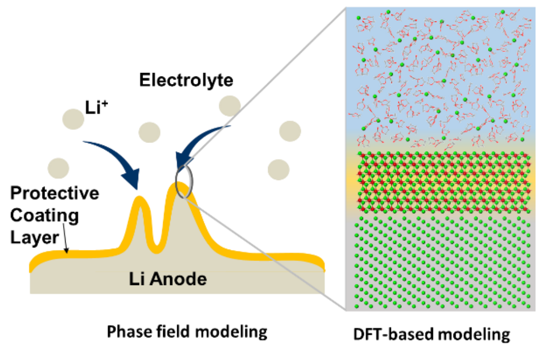
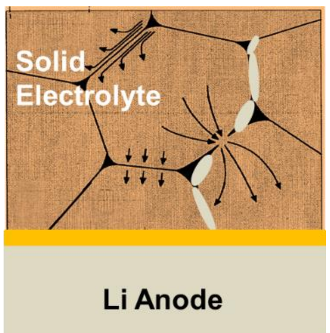
Acknowledgements

- Patricia Smith, Tien Duong, and Walter (Jerry) Parker for program management.

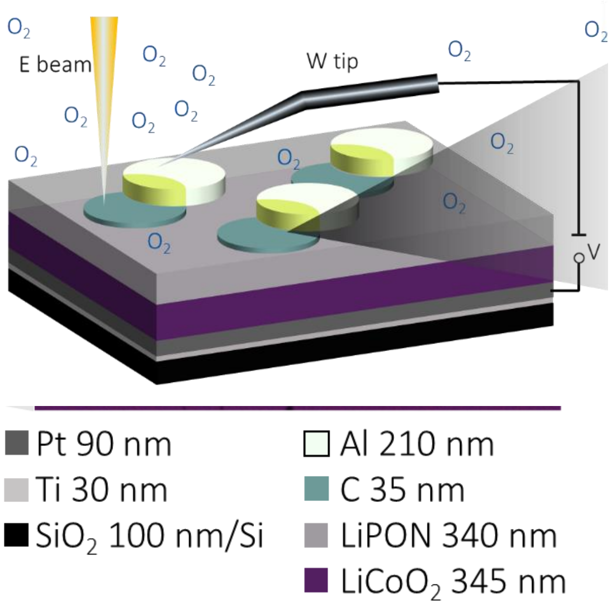
- Dr. Yunsong Li, MSU, (Li/SEI/liquid electrolyte atomistic modeling)
- Zhe Liu, PSU, (phase field development and modeling)
- Hong-Kang Tian, MSU, (solid electrolyte DFT modeling)
- Jiagang Xu, GM, (experimental work).

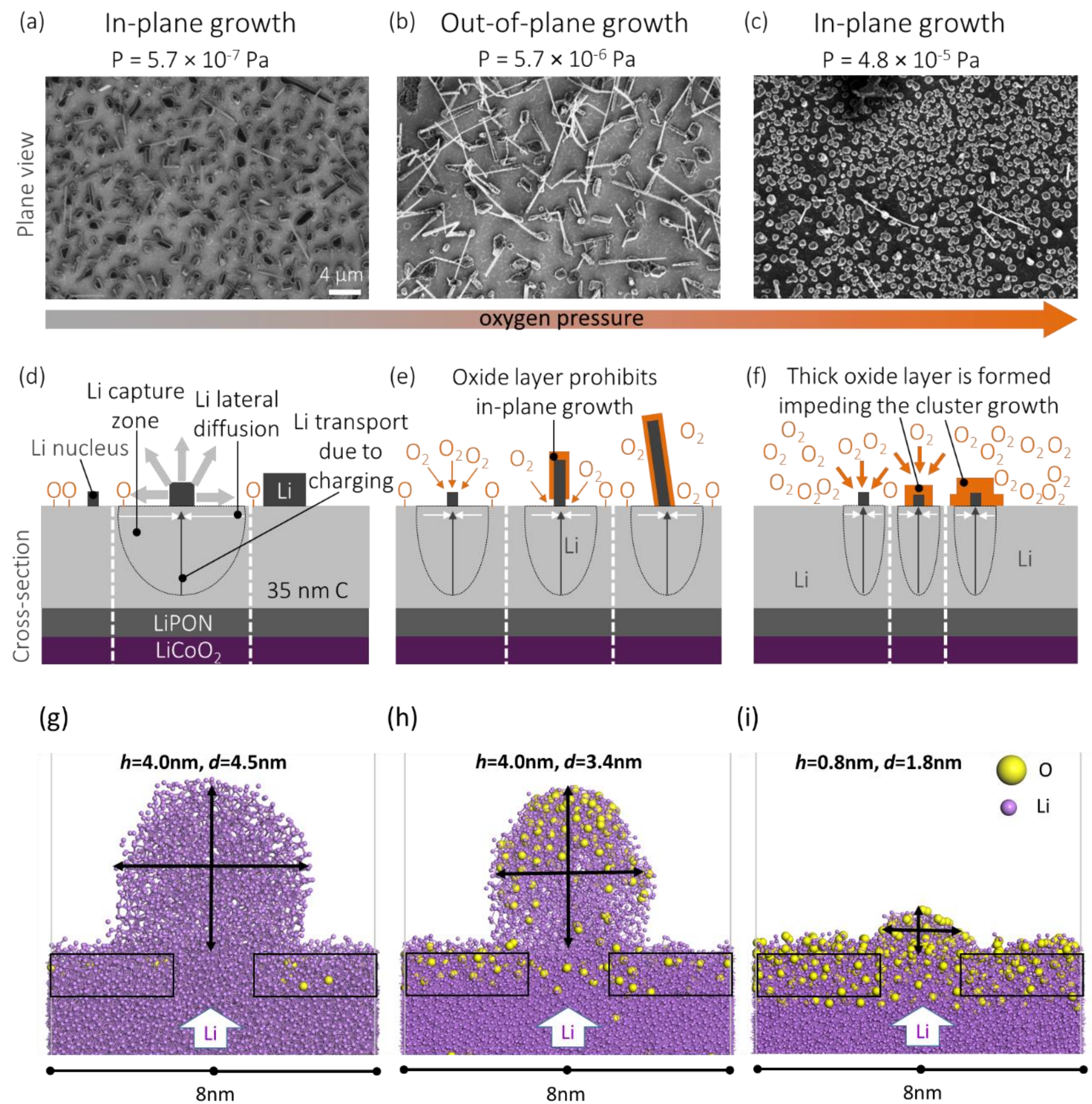
BACK UP SLIDES

Compare liquid and solid electrolyte to understand the role of SEI in dendrite growth

	Growing in liquid electrolytes	Growing in solid electrolytes
Knowledge Transfer	→ The effect of the nm-thick protective SEI layer (exist in both) The effect of the microstructure (easier for experiment) ←	
Key phenomena		
Key questions	The effect of the nm-thin SEI The relationship with the separator porous and mechanical structure	The growth mechanism in mm-SE. Mechanical confinement from the pore and weak interfaces in SE.
Common	Common components in the SEI at Li/electrolyte interface: such as Li_2O	
Similar situations	Polymer electrolyte at high temperature (T)	polymer electrolyte at low T
Different Atomistic Details	Li^+ and e Transport at the Li/SEI/liquid-electrolyte interface	Li^+ and e transport at the SE surface and boundaries
Phase-field model similarities	Governing equations, Butler-Volmer kinetics, Charge carrier (electron and Li-ion) transport, include microstructure details, track microstructure evolution	

The passivation layer changes the morphology of Li





Reactive MD simulation

Not exact the same as SEI
But Li_2O is an important component in SEI

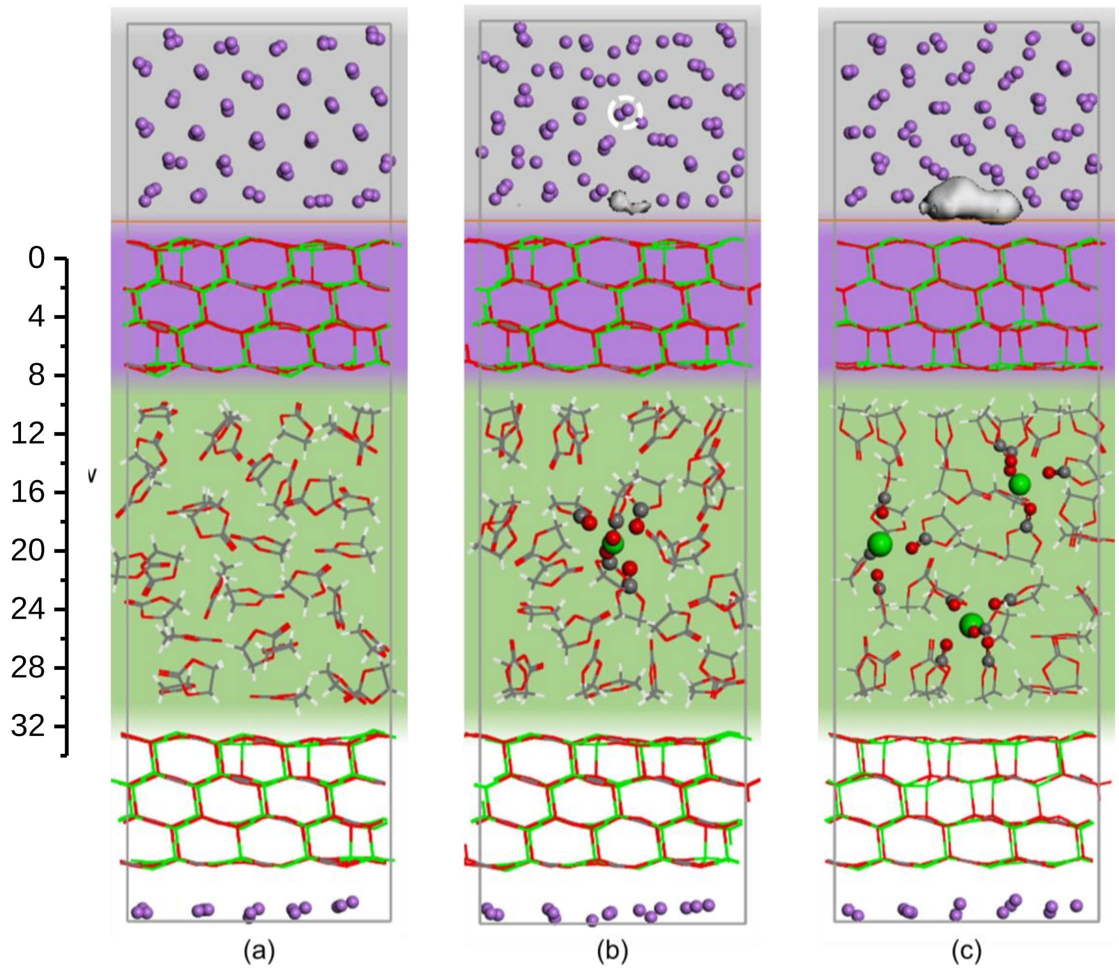
Nano Letter (2018)

*A. Yulaev, V Oleshko, P Haney, J. Liu, **Y Qi,** A. Talin, M.S. Leite, and A. Kolmakov*

DFTB Simulation of the Reduced and Oxidized States

σ=0 σ=-0.14 σ=-0.42 e/nm^2

Excess electron density (σ)



4 layers of Li_2CO_3

Charge on Li^+ ~ +0.6

Ignored the background charge from $Li^+ \cdots PF_6^-$ pairs

Typically
1M $LiPF_6$ in EC/DMC

Reduced Oxidized

Overall neutral system, DFTB molecular dynamics